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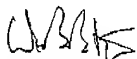
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MESSAGE

Examiner Noguerola,

Attached, as requested in your voice mail message on Friday, December 19, 2003, is a copy of the Seers reference (listed as reference CY in our IDS) and the English language statement regarding the Midgley reference (Midgley D. and Torrance K. (1991) Potentiometric Water Analysis. J. Wiley & Sons, listed as reference DV). I also approve the insertion of the word "electrode" after the word "reference" in claim 1, line 4 and claim 7, line 5 as you suggested. You are authorized to insert these words in an Examiner's Amendment, if you so choose. If you have any further questions regarding this case, do not hesitate to call. Best regards and happy holidays.



William B. Batzer
USPTO Reg. No. 37,088

SCHLUMBERGER TECHNOLOGY CORPORATION

AN INSTRUMENT FOR SIMULTANEOUS MEASUREMENT OF Eh AND pH IN BOREHOLES

K.J. Seers

An instrument is described that measures Eh and pH simultaneously in boreholes. The temperature of the borehole fluid and its self-potential with respect to an up-hole mud probe can also be measured. Operation should be possible in water depths to 100 m. By connecting the pH electrode system in a feedback circuit, electrometer amplifier performance is obtained from a cheaper, lower quality amplifier.

Signal subtraction operations allow the same reference electrode to be used simultaneously for all measurements. Sources of error are reduced by careful guarding of the high-resistance input circuits and by using isolation amplifiers to prevent ground leakage currents. A number of future development possibilities are indicated.

Introduction

A prototype field instrument, the KEP-1 Eh-pH probe, has been developed by BMR for simultaneous in situ measurements of pH, Eh (oxidation-reduction potential), temperature, and SP (self-potential) in boreholes. Applications are in groundwater studies related to weathering, orebody formation, waste disposal, etc.

Unlike instruments previously reported in the literature (Back & Barnes, 1961; Bolviken & others, 1972; Mann, 1974), the KEP-1 uses industrial-type electrodes capable of withstanding pressures of 1034 kPa (150 psig) and so does not require a pressure-compensating mechanism for operation down to a water depth of 100 m. Furthermore, the circuitry developed for the KEP-1 ensures no observable interactions between simultaneous pH, Eh, and SP measurements, even though the common reference electrode is in the feedback circuit of the amplifier that measures pH. The ability to log all variables simultaneously simplifies field operations and guarantees accurate measurement correlation.

Measurement of pH

In conventional pH measurements the high resistance glass electrode connects to an electrometer amplifier and the reference electrode connects to signal ground. An electrometer amplifier is necessary because of its high input resistance ($> 10^{13}$ ohm), which prevents the flow of current through the glass electrode; also the input bias current required by an electrometer amplifier is very low (typically $< 10^{-14}$ amp), which ensures that electrode polarisation is negligible and solution potentials are unaffected. Such amplifiers are usually of hybrid rather than monolithic construction and so are more bulky and difficult to package in a slim probe; they are also expensive to replace if the probe is damaged or abandoned.

Figure 1 shows how a relatively cheap FET-input monolithic amplifier (Analog Devices AD545JH) is used in the KEP-1.

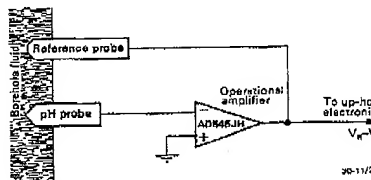


Figure 1. pH measurement

The amplifier is connected in a unity-gain inverting circuit, with the cell comprising the reference and pH electrodes forming the feedback path. This amplifier's open loop input resistance (10^{13} ohm) is thus effectively multiplied by its open loop gain (2×10^7) to give an effective input resistance of 2×10^{20} ohm. Bias current is less than 2 pA at 25°C, doubling for every 10°C increase; this is comparable with input currents specified in commercial pH meters. The glass electrode (Leeds & Northrup 117839) has a sensitivity of -59.16 mV per pH unit, and the maximum error caused by bias current flowing in the 77 Megohm electrode circuit is, therefore, 0.0026 pH unit at 25°C. The reference electrode (Leeds & Northrup 117481) is a diffusion type with saturated KCl gel electrolyte and Ag-AgCl internal element.

In Figure 1, if the half-cell potentials developed on the pH and reference electrodes are V_P and V_R , respectively, the amplified output is $V_R - V_P$, because $V_R - V_P$ is zero at a nominal pH of 7, the KEP-1 system adds in a fixed voltage so that the analogue pH output range of 0-11 volts corresponds to 0-11 pH.

Gain and offset in the pH-measuring circuits are adjusted by front panel 'slope-correction' and 'standardise' controls that enable calibration with two buffer solutions of known pH. For recording small variations, an 11-position offset switch is provided to back off integral numbers of pH units, and a $\times 10$ gain switch increases the sensitivity for the residual fraction. Resolution is 0.001 pH unit; whether this is significant depends only on the repeatability of the electrode system, which is still under evaluation.

The initial plan was to compensate for the temperature coefficient of the glass electrode with a temperature-dependent resistance in the form of an automatic temperature compensation (ATC) probe (Leeds & Northrup 152137). However, in

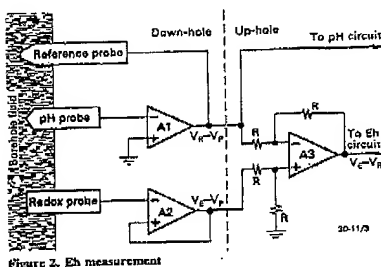


Figure 2. Eh measurement

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the prototype, the ATC probe is used to measure temperature directly and the data are subsequently corrected for the glass electrode characteristic. The temperature of the borehole fluid can be measured to within 0.1°C , by passing a constant current through the ATC probe and measuring the voltage developed. An improved design is planned to include both temperature measurement and automatic compensation.

Measurement of Eh

A gold-tipped platinum redox electrode (Leeds & Northrup 117419) forms the measurement cell with the reference electrode used for pH measurement. The redox electrode connects to an amplifier of the type used for pH measurement; low bias current and high input resistance again ensure low errors. Figure 2 shows the analogue subtraction method used to obtain Eh.

If V_p is the half-cell potential across the glass electrode, the fluid may be considered to be at a potential of $-V_p$ with respect to signal ground. Thus, if the redox electrode half-cell potential is V_R , the output of amplifier A2 is $V_R - V_p$. The output of amplifier A1, $V_R - V_p$, is subtracted from this by amplifier A3 to give $V_R - V_R$, the potential that would be developed across the cell formed by the redox and reference electrodes alone.

This subtraction would be unnecessary if the connections to the pH and reference electrodes were reversed: the output of A2 would be $V_R - V_p$ directly. However, when tried, this configuration produced scatter in both Eh and pH readings. The cause of this has not been definitely established; it is likely that spurious solution potentials cause currents to flow in the high resistance glass electrode via the amplifier's low output resistance. Such currents would be negligible with the glass electrode connected to the high resistance input of the amplifier.

The instrument multiplies $V_R - V_p$ by ten to give an analogue output of 1 volt per 100 millivolts Eh. Resolution is better than 1 mV Eh, but whether this is meaningful again depends on electrode constancy. The potential of the reference electrode (0.1985 V at 25°C) must be added to obtain the Eh value.

SP measurement

In principle, there is no limit to the number of electrodes that can be referred simultaneously to the one reference electrode, using the subtraction scheme outlined above. The only constraint is that any current drawn from the fluid by an electrode or its associated amplifier must be low enough to avoid errors in the potentials measured by the other electrodes. SP is, therefore, measured in the same way as Eh.

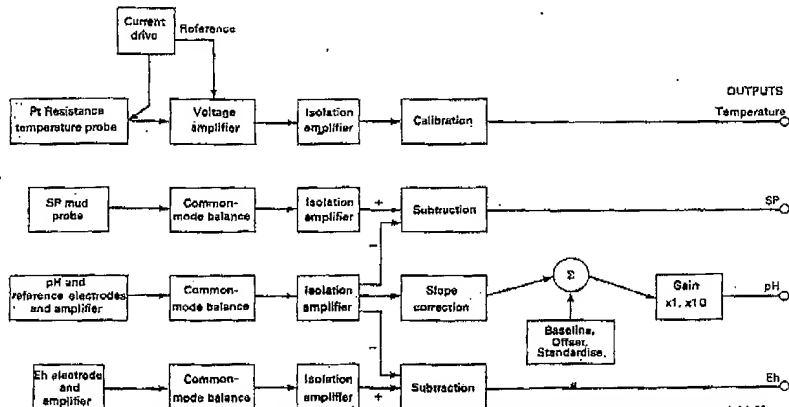
The SP electrode is a mud probe in the ground near the top of the borehole. A circuit similar to that in Figure 2 gives the potential developed between the probe and the down-hole reference. Output range and scale factor are as for Eh.

Ground isolation

It has been shown that the borehole fluid must be considered to be at a potential of $-V_p$ with respect to signal ground. This sets a stringent requirement for no ohmic connection between signal ground and the fluid, i.e., between signal ground and the actual ground — a requirement not easily met in field situations, where the recording system or its power supply can readily develop leakage paths to ground. Leakage of only $0.5 \mu\text{A}$ flowing in the reference electrode could produce an error of 0.1 pH; an ohmic path of 10^9 ohm resistance between signal ground and the borehole fluid would almost halve the pH indication.

To avoid problems of this nature, all signals from the down-hole probe and the SP mud probe are passed through isolation amplifiers with carefully guarded inputs in the up-hole electronics unit. These amplifiers also provide isolated power supplies for the down-hole electrodes. Each amplifier (Analogue Devices 284J) has a minimum isolation resistance of 5×10^{10} ohm.

Because the probe cable is immersed in the fluid, its insulation must be of very high quality, electrically and mechanically. Long-term cable reliability has still to be investigated.



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To guard against the possibility of errors caused by common-mode voltages induced in the long probe cable, common-mode balancing circuits are included at the input side of the isolation amplifiers.

Figure 3 is a simplified block diagram of the complete instrument.

Physical configuration

Figure 4 is a photograph of the down-hole probe and up-hole electronics unit. The down-hole probe contains the pH, redox, and reference electrodes and the ATC probe. These are mounted with O-ring seals in a polycarbonate cylinder, designed to allow rapid displacement of entrapped air by the borehole fluid and to ensure free fluid flow around the electrodes. Amplifiers A1 and A2 (Fig. 2) are mounted in the upper part of the probe on a copper disc that forms part of the input guard. Probe length is 40 cm and its diameter is 6 cm. This is larger than necessary, because the original design included a pressure-compensating piston system as described by Mann (1974). This is not now considered necessary for water depths to 100 m.



Figure 4. KEP-1 Eh-pH probe

The up-hole electronics are housed in an aluminium instrument case of approximate dimensions 30 cm x 23 cm x 13 cm. Simultaneous outputs of pH, Eh, SP, and temperature are provided for separate meters or chart recorders. The system operates from 12V d.c. and draws approximately 0.34 A. The probe is connected by six-core well-logging cable and a standard well-logging connector.

Proposed developments

The prototype has operated successfully in laboratory tests and in a bore-hole where depth has been limited to 45 m so far. After further testing and evaluation, the following improvements may be incorporated: automatic temperature compensation for the glass electrode, pressure and conductivity measurements, digitising and multiplexing all down-hole signals onto a single core, digital readout and, possibly, digital recording, reduction of probe dimensions.

Acknowledgements

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References

- Back, W., & Barnes, I., 1961 — Equipment for field measurement of electrochemical potentials. *United States Geological Survey Professional Paper 424-C*, C366-C368.
- Bolviken, B., Logn, O., Breen, A., & Udda, O., 1972 — Instrument for in situ measurements of Eh, pH and self-potentials in diamond drill holes. *Geochemical Exploration 1972*, (London), *The Institution of Mining and Metallurgy*, 415-420.
- Mann, A., 1974 — Down-hole Eh-pH and water sampler. *CSIRO Minerals Research Laboratories, Report No. FP 5*.

[2] English Statement

The book is dedicated to a problem of the analysis of water, actual owing to limitation of its resources, and necessity it durable for needs of an industry, agriculture, household requirements. The potentiometric method, considered in the book, of the analysis is one of the most effective ways of definition of the contents in water of inorganic matters.